

EXP 131

31 January 1954  
Copy No. 15 of 40

PRELIMINARY STUDIES LEADING TO THE DEVELOPMENT  
OF A SUBMERGED COMBUSTION BOILER

TM - 577

Final Report

Gerald Golub

EXPERIMENT INCORPORATED  
Richmond 2, Virginia

Prepared for the  
OFFICE OF NAVAL RESEARCH  
covering work performed under Contract  
N0nr-1149(00)

## CONTENTS

	<u>Page</u>
Contract Fulfillment	3
Summary	4
Introduction	5
Literature Survey	6
Industrial Survey	9
Experimental	10
Recommendations for Future Work	12
Conclusions	13
References	14
Distribution List	23

### CONTRACT FULFILLMENT

This report is submitted as fulfillment of the detailed technical report requirement under Contract NONr-1149(00) for the period February 1, 1953, to January 31, 1954, which provides for (1) a survey of the chemical and engineering literature to ascertain the present state of knowledge in regard to high-temperature liquid systems and a compilation of a list of materials of potential interest for the proposed application; (2) the contacting and visiting of organizations having information pertaining to the materials uncovered in (1) above in order to accumulate all available technical data related to the intended use; and (3) the subjecting of promising materials uncovered in the course of (1) and (2) above to simple but adequate laboratory tests to determine the effect of ordinary combustion gases on the material over the temperature range of interest.

## SUMMARY

In order to investigate non-volatile materials as possible heat-transfer media in a submerged combustion-type boiler, the problem was divided into three phases, namely, a literature search, an industrial survey, and a laboratory evaluation of the materials found in either the literature search or the industrial survey.

Literature Survey. The more comprehensive catalogued sources of information, such as the Chemical Abstracts, were searched for data on high-temperature liquid systems. Of the many systems mentioned in the desired temperature range ( $200^{\circ}$  to  $2000^{\circ}\text{F}$ ), none were completely suitable for the proposed application. In view of this fact, a general set of physical and chemical requirements for the needed system was formulated. Materials must (1) be liquid over an extended temperature range, (2) have a low vapor pressure in the vicinity of  $900^{\circ}\text{F}$ , (3) be chemically and physically stable to the products of combustion, and (4) be easily and safely handled.

Two types of molten or liquid substances were encountered in this temperature range. Those systems which were characterized by low-melting glasses not only had high viscosities near their melting points but their transition from solid to the liquid state was slow and not clearly defined. For example, boron trioxide has a melting point of  $845^{\circ}\text{F}$  but has an estimated viscosity of 10 poises at  $1200^{\circ}\text{F}$  (glycerol at  $77^{\circ}\text{F}$ ) and one centipoise at  $1650^{\circ}\text{F}$  (water at  $77^{\circ}\text{F}$ ). Such substances were difficult to melt in their entirety. The other materials had much lower viscosities near their melting points, and as a result, these substances melted faster. For example, a molten chloride eutectic, consisting of 46.5 mol per cent  $\text{LiCl}$ , 42 mol per cent  $\text{KCl}$ , and 11.5 mol per cent  $\text{NaCl}$ , has an estimated viscosity of 4 to 7 centipoises. Other materials, such as the nitrates, carbonates, hydroxides, phosphates, and sulfates, do not appear to be suitable as the heat-transfer medium because of chemical instability. However, systems in a state of continual equilibrium, such as a carbonate-oxide-hydroxide system, might be acceptable.

Industrial Survey. The main industrial uses for stable salt baths are in the metallurgical industry for the heat treatment of metals and in the chemical industry to replace steam as a heating medium. In view of the necessary requirements for chemical stability and liquid properties, none of the industrial baths were suitable. From inquiries to many industrial manufacturers it was confirmed that no organic compound or pure metal would be stable in the desired temperature range.

Laboratory Tests. When materials were uncovered that appeared promising, they were first melted in porcelain crucibles and then subjected to the hot combustion gases in a laboratory-type submerged burner. Six different materials were tested, but only three were actually subjected to the hot combustion gases. The fluorides, metaphosphates, and carbonates did not

look promising after the crucible test. The nitrate-nitrite material was converted to the carbonate, whereas the boron trioxide did not circulate properly, as it was too viscous. The chloride eutectic appeared stable to the combustion gases and operated satisfactorily as the heat-transfer medium in these small-scale tests.

### INTRODUCTION

As a result of the suggestions by Experiment Incorporated to the Office of Naval Research and the Bureau of Ships on a novel approach to the problems of high-output steam generators, a program was initiated at Experiment Incorporated to determine a suitable material to serve as the heat-transfer medium.

The usual method of transferring heat in a conventional boiler employs a gas-solid interface. This gas-solid interface has a comparatively low over-all coefficient of heat transfer, which for any system requires both large temperature differences and large surfaces. In fact, in most boilers large temperature differences are maintained over the majority of the tube surfaces. This new approach consists of transferring heat from the combustion gases to a molten salt or other liquid by exhausting a burner beneath the surface of the liquid, by passing the combustion gases through a spray of the liquid, or some advantageous combination of both methods. This liquid or molten salt is then used to transfer heat to the steam or water tubes of the generator, thus substituting a liquid-solid interface for a gas-solid interface. Preliminary design calculations have indicated that such a process would enable steam generators to be lighter and smaller than the conventional generators of comparable output and efficiency.

This heat-transfer material should possess the following physical and chemical properties:

- (1) a low vapor pressure at 900°F;
- (2) a melting point as far below 900°F as possible;
- (3) a liquid over an extended temperature range;
- (4) chemically and physically stable to the products of combustion;
- (5) a good heat conductor;
- (6) inexpensive and readily available;
- (7) easily and safely handled.

Previously, the applications of high-temperature liquid systems were confined to the fields of metallurgy and ceramics. The metallurgist used these liquids to heat-treat metals; and the ceramist used non-metallic materials, usually compounds represented by a mixture of oxides, to make wares of various kinds. Recently, the chemical industry has begun to use molten salts as heat-transfer media in closed systems up to 850°F (1), but high-temperature systems of the type required in this application have not been developed. In view of these facts, industry has few of the required specific or experimental data on these materials; however, it is clear from the periodic table that a system of this type must be chosen from substances containing the following elements: B, N, O, F, Cl, Br, I, C, As, P, Si, and S. Therefore, the actual problem consists of sorting and eliminating the compounds and mixtures of compounds of the above elements by searching the literature, contacting industry, and making simple experiments on the more promising compounds or mixtures of compounds found by the first two methods.

### LITERATURE SURVEY

Submerged combustion has been practiced since the days of Collier in 1887. Investigators have attempted to increase the over-all heat-transfer coefficients by eliminating the gas and water films at the boiler shell by actually burning the fuel in the steam space below the surface of the water, and allowing the products of combustion to bubble through the water, thereby eliminating both the metal retaining wall and the gas-solid interface.

In such pieces of apparatus as the plate or dephlegmator columns, the Porlan, and gas scrubbing towers, high heat-transfer rates are realized because of the elimination of these gas-to-solid-to-water interfaces. Moore (2) has presented a review of the early workers in this field. Hammond (3) found that the effective surface area of combustion gases bubbled through the heating medium (water, oil, or salt) is on the order of 1-1/2 acres per cubic foot of gases. In view of this enormous surface area, a temperature equilibrium is established quickly, thus eliminating any hot spots in the heated solution. Since only a small fraction of the heat is lost to the surrounding shell and the remainder of the combustion gases give up their heat to the liquid, these burners are extremely efficient.

This method was not acceptable for generating steam because of the presence of non-condensables in the steam and the necessity for pressurizing the fuel and air to the pressure of the steam drum. Thus, the submerged burner has been limited to the evaporation of solutions that are heat sensitive, extremely viscous, cake, or form scale on the evaporating surfaces (2).

In order to eliminate these objections, it was planned that the burning would be carried out in a stable, non-volatile liquid where the loss of the heat-transfer medium would be small. The boiler tubes would pass through this

medium and thereby effect large heat-transfer gains.

High heat-release burners on the order of 2 million Btu per ft<sup>3</sup> of combustion space were developed for jet-propulsion applications. This compares with 150,000 Btu per ft<sup>3</sup> for general use and 450,000 Btu per ft<sup>3</sup> in the high-performance U. S. Navy boiler. Capacities sixteen times greater than the present U. S. Navy boiler are in sight because of the large increase in the rates of heat transfer and the use of high-output burners.

High-temperature Liquid Systems have been studied by Hall and Insley (4), who have compiled a great many of the available phase diagrams for the use of the ceramist, and O'Keefe (5) has compiled the composition of 75 typical salt-bath solutions for the use of the metallurgist and the engineer. Although these two sources contain most of the work on reported high-temperature systems, Chemical Abstracts has reported various other liquid systems which might be of interest. Table I presents a compilation of promising substances.

Oxides have been studied extensively by Brewer (6) and others, but Brewer presents the latest compilation. If one eliminates those compounds that (a) react with water to form hydroxides, or carbon dioxide to form carbonates, (b) melt above 900°F, (c) have an appreciable vapor pressure at 900°F, or (d) are unstable, only B<sub>2</sub>O<sub>3</sub> will remain. Boron trioxide melts at 842°F, does not react with carbon dioxide, has a vapor pressure of 10<sup>-3</sup> atm at 2200°F, and boils at 4550°F (6). Kracek, et al. (7), Speiser, et al. (8), and Southard (9) have reported similar values. Although boric anhydride forms several acids in the presence of water, at temperatures above 900°F these acids are dehydrated. Boric anhydride is a member of an exceptionally stable oxide group. Jenckel (10), Mazelev (11), Hall and Insley (4), Leon'eva (12), Gmelin (13), Foex (14), Geller and Bunting (15), Eubank and Bogue (16), Cole and Taylor (17), Potts (18), Toropov and Kononov (19), Knight (20), Davis and Knight (21), Dane (22), Levi and Curti (23), Jaulmes and Gontard (24), Jaulmes and Galhac (25), and others have investigated the system of B<sub>2</sub>O<sub>3</sub> plus other oxides. All of the studied systems show only a small lowering of the melting point of B<sub>2</sub>O<sub>3</sub> by other materials. The data and equations of Kobeko, et al. (26) and Leont'eva (12) indicate that the viscosity of B<sub>2</sub>O<sub>3</sub> is 10 poises (glycerol at 77°F) at 1230°F and one centipoise (water at 77°F) at 1750°F. These data show the need to reduce the viscosity of the B<sub>2</sub>O<sub>3</sub> before it can be used. Stalhene (27) has shown that Na ions lower the viscosity, but not to the levels desired. (More work could be done here.) Such investigations as reported by Hackspill and others (28), Thome and Ward (29), Badger and Pittman (30), Lux (31), Vargin (32), Todd and Miller (33), and Roth and Barger (34) are also of interest.

Chloride Systems have been reported by Hall and Insley (4) and others. In the metallurgical industry (5) chlorides are used in baths for high-speed steels, alloy carbon steels, and stainless steels in the temperature range 500°-2400°F. They usually consist of mixtures of NaCl, KCl, BaCl<sub>2</sub>, NaF, Na<sub>2</sub>CO<sub>3</sub>, NaCN, CaCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, ZnCl<sub>2</sub>, plus small amounts of TiO<sub>2</sub> and SiO<sub>2</sub>, depending upon the temperature requirement of the specific salt bath, e.g.,

quenching, tempering, nitriding, etc. Adadurov (35) demonstrated the existence of catalytic decomposition of NaCl and KCl by such metals as Mo, W, Cd, Zn, Cu, V, and Fe from 572° to 932°F. Guthrie and Nance (36) measured the decomposition of alkali metal chlorides by passing air through the molten salt at 1500°F for 30 minutes. He reported that 1.0, 0.06, 0.03, and 0 per cent LiCl, NaCl, KCl, and CsCl, respectively, were decomposed, but that the concentration of water in the air had some effect. When superheated steam at 1350°F was passed through LiCl for 30 minutes, 10 per cent decomposed. Kersten (37) has patented a process for HCl manufacture based upon the decomposition of alkali halides by steam in the presence of silicates. Bichowsky (38) shows that LiCl is not decomposed by evaporating water from LiCl solutions. These experiments were probably carried out in the temperature range 250°-300°F. If a reasonable temperature exponent for the rate of decomposition is assumed, at a maximum desired temperature of 900°F a chloride eutectic should have a fairly long life. Hackspill and others (28) have shown that hydrochloric acid is driven from chloride baths with the addition of B<sub>2</sub>O<sub>3</sub> at temperatures of 212-302°F. Lowry (39) and co-workers present evidence for the complete ionization of molten chlorides. The stability of liquid chlorides in the presence of steam will depend largely on the hydrolysis constant of the particular chloride salt. A calculation of the equilibrium constant for the formation of hydrochloric acid in the above bath at 77°F from the thermodynamic data of Bichowsky (38) and Glasstone (40) gives the value  $1 \times 10^{-18}$ , which is almost negligible. The tendency of chloride salts of weak bases to decompose is inversely proportional to the strength of the specific base, as demonstrated by the work of Domange (41) with fluorides. In industry those baths containing salts of weak bases are rectified with acid or compensating mixtures (42). In view of these facts, only salts of strong bases will be considered. Kayser (43) presents the work of Sanders (44), who developed a chloride bath with an operating range of 80° to 1500°F in a closed system. Since this bath, called NS fluid, contains chlorides of the weak bases, iron and aluminum, both air and water decompose it rapidly. It is interesting to note the favorable heat-transfer characteristics of this salt mixture. The specific heat is 0.7 Btu/lb-°F, the density is 126 lb/ft<sup>3</sup>, and the heat transfer coefficient is 23.6 Btu/ft<sup>2</sup>-°F-hr in the temperature range of 300° to 1500°F. According to the data of Kangro and Wiekling (45), Mayer and Wintner (46), and Stull (47), the vapor pressure of mixtures of NaCl, LiCl, and KCl at 900°F is small, much less than 1 mm of Hg. At ordinary temperatures NaCl is an isopiestic standard because of its low volatility (48). The viscosity of molten chlorides is about 4 to 7 centipoises around 750°F. It is interesting to note that the oxide systems have high viscosities for several hundred degrees past their melting points (27), whereas the viscosities of the chloride salts decrease rapidly once past their respective melting points (49). Further pertinent information can be found in the papers of Rasninskaya and Bergman (50), Elchardus and Laffitte (51), Olander and Liander (52), Leitgeb (53), Keitel (54), Johnson (55), Ipatov (56), Villa (57), Sato and Amano (58), Shearon (59), Sanders (44), Samuel (60), and Salstrom (61).



Other Halogens are not as well suited as the chlorides, as they have higher melting points (fluorides) (62) or their tendency to decompose by hydrolysis is much greater (iodides, bromides) (40). However, small quantities of the other halide salts may help lower the melting point and increase the fluidity and stability of a particular eutectic mixture.

Nitrates. The use of nitrates in salt baths has been studied extensively by Kirst, et al. (1) and others. These baths are characterized by their low-melting points, around 250°F, stability in closed systems free of carbon dioxide, and low-corrosion rates, but they are readily converted to their corresponding carbonates by intimate contact with hot carbon dioxide (63).

Carbonates form eutectics around 930°F (64). The dissociation pressures of  $K_2CO_3$ ,  $Na_2CO_3$ , and  $Li_2CO_3$  at 2200°F are, respectively, 27, 41, and 300 mm of Hg. At 1470°F,  $K_2CO_3$  has a dissociation pressure of less than one mm of Hg (29); however, in view of the ease with which water releases carbon dioxide from carbonates, these materials will decompose rapidly. There is a 13 per cent loss of  $CO_2$  when a solution of  $Na_2CO_3$  is boiled for 24 hours (29).

Inasmuch as the stable borates, phosphates, arsenates, silicates, and sulfates melt too high to be of practical use, they were not studied in detail. The organic compounds, including the new fluorine and silica derivatives, all have high vapor pressures in the desired temperature range (65). All pure metals would in time be chemically converted to their oxides (66).

Equilibrium Studies which are constantly changing--i.e., in dynamic equilibrium--might be useful. For example, a eutectic of  $Na_2CO_3$ ,  $K_2CO_3$ , and  $Li_2CO_3$  would in time partially decompose to  $Na_2O$ ,  $K_2O$ , and  $Li_2O$ . Then the water from the combustion process would convert these oxides to hydroxides, and these hydroxides plus carbon dioxide would form carbonates, thus completing the cycle. After a system once came to equilibrium, it would have a least nine different components; and by adjusting the temperatures in the various parts of the bath by drawing off steam, or changing the products of combustion by using different fuels, or changing the fuel-air ratios, the system could be maintained in any given equilibrium condition. The necessary data to calculate these equilibriums are being collected.

## INDUSTRIAL SURVEY

Table II presents the results of the letters sent to 35 firms employing, manufacturing, or associated with high-temperature (500°-1100°F) liquid heat-transfer media. The pertinent data obtained are presented elsewhere. From this survey it is evident that industry has developed only a limited number of systems suitable as heat-transfer media in this temperature range. In the vicinity of 900°F the chemical industry uses mainly the nitrate-nitrite salt eutectic mixtures (1), whereas the metallurgical industry has

several different baths for use at this temperature. None of them, however, will satisfy the stability requirements because of one or more of their components. The ceramics industry's interest in high-temperature liquid systems is limited to those involving glasses, clays, or other ceramic materials. These materials usually have high melting points or high viscosities (4).

Manufacturers of substances that showed promise from the literature survey were consulted on the properties of their particular substances to gain additional knowledge of these materials.

### EXPERIMENTAL

The purpose and plan of the investigation was to uncover a liquid medium which would be stable while in intimate contact with ordinary combustion gases at 900°F. A laboratory-type submerged burner was operated beneath the surface of these liquids; however, the materials were melted in porcelain crucibles and their liquid properties noted before subjecting them to the operating burner.

Materials used for this investigation are described below. The nitrate salts were purchased from the Crown Chemical Corporation of Branbury, Connecticut. This salt is designated as Crown T-1 Tempering Bath Salts and consists of 40 wt per cent  $\text{NaN}_2$ , 7 wt per cent  $\text{NaNO}_3$ , and 52 wt per cent  $\text{KNO}_3$ . Pulverized boric acid, technical grade (A-100), was obtained from Phipps and Bird Company, of Richmond, Virginia, and the pulverized boric acid, anhydrous, was a 5-lb sample from the Pacific Coast Borax Company, a division of Borax Consolidated Ltd., 510 West 6th Street, Los Angeles, California. Lithium chloride, pure; lithium fluoride, c.p.; potassium chloride, c.p.; potassium chloride, technical; and sodium fluoride, technical, were purchased from the Fisher Scientific Company, of Washington, D. C., and the sodium chloride was ordinary household table salt purchased at a local grocery.

The apparatus used is shown in Figure 1, a schematic drawing of the liquid-salt testing apparatus. Figures 2 and 3a are actual photographs of the equipment. The burner is a nozzle-mix laboratory submerged burner manufactured by the Submerged Combustion Corporation of America at Hammond, Indiana. The heater is a 1250-watt Calrod Tubular Heater, Catalog Number 4H/21G2, manufactured by the General Electric Corporation. The coiled copper tubing is standard 1/4-in. copper tubing. The remaining burner parts were fabricated at Experiment Incorporated. The 50-ml porcelain crucibles were obtained from the Arthur H. Thomas Company, of Philadelphia, Pennsylvania, Catalog Number 4122.

The procedure followed in the investigation is described below. The promising materials were subjected to a crucible test which consisted of melting these substances in a porcelain crucible over a Bunsen Burner. The

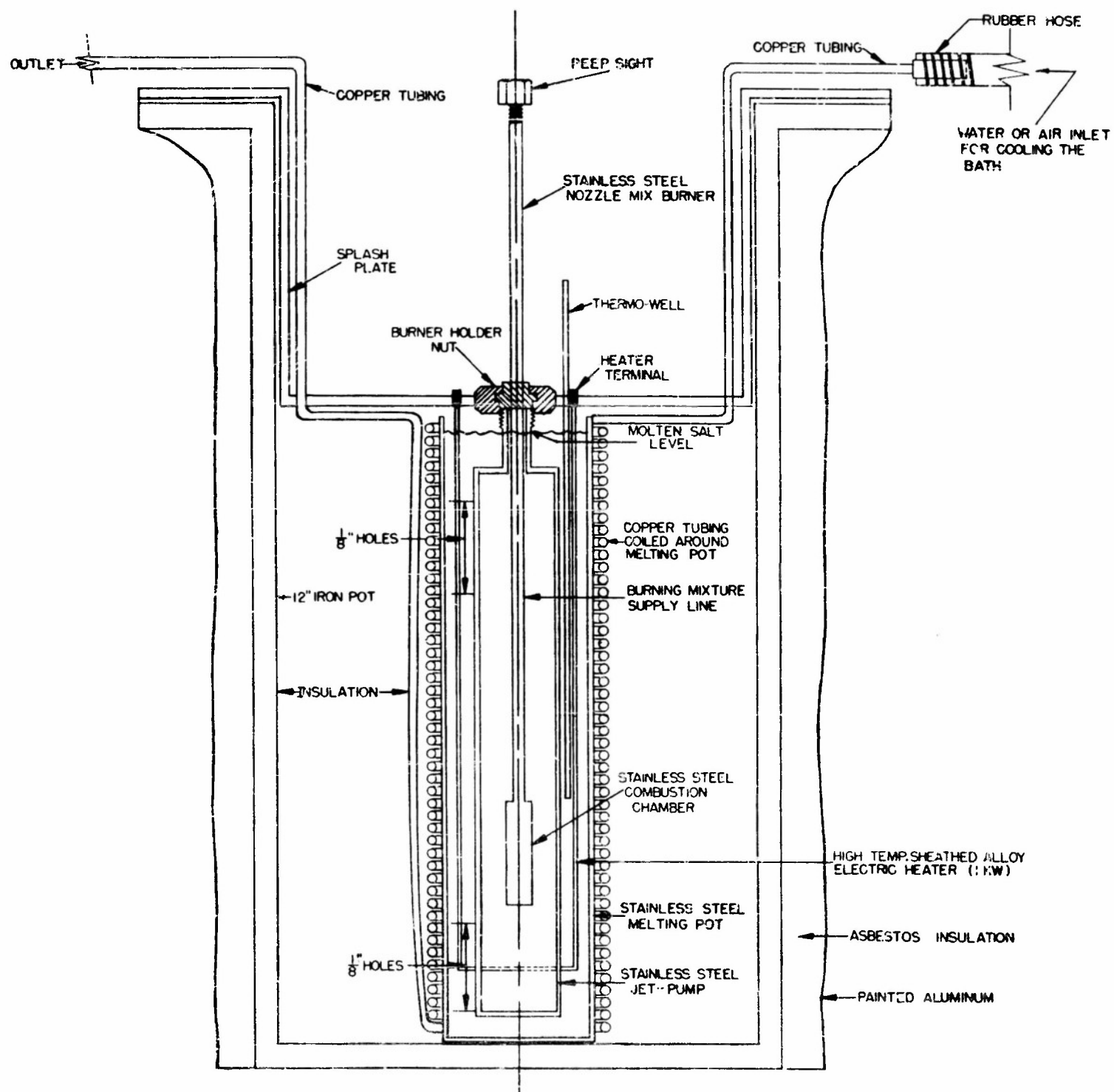
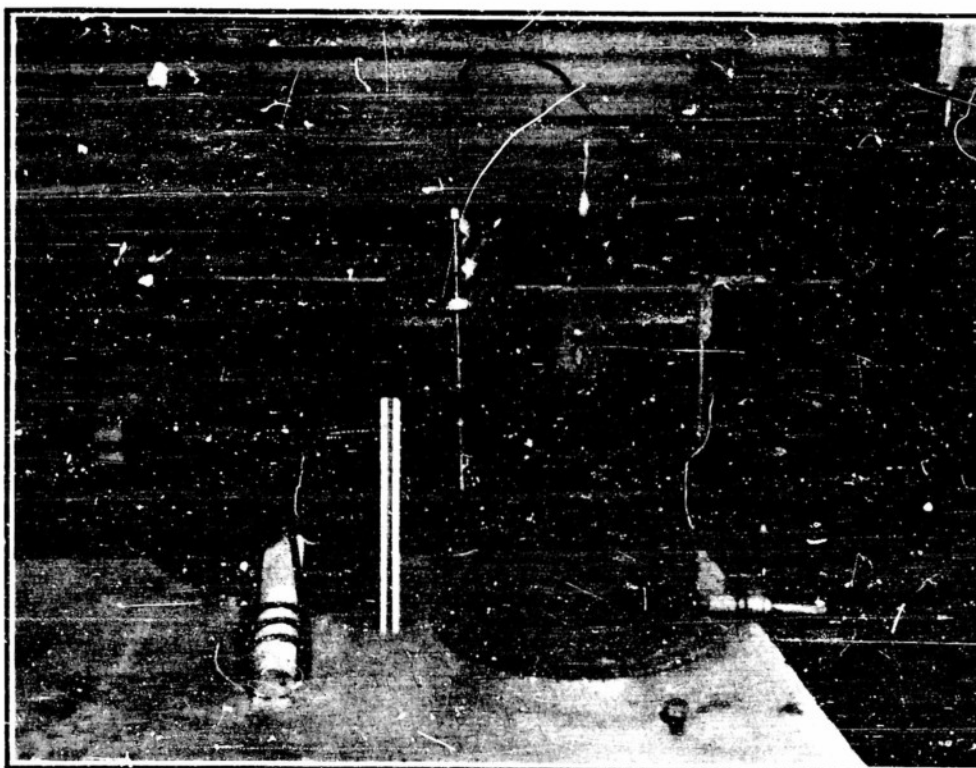
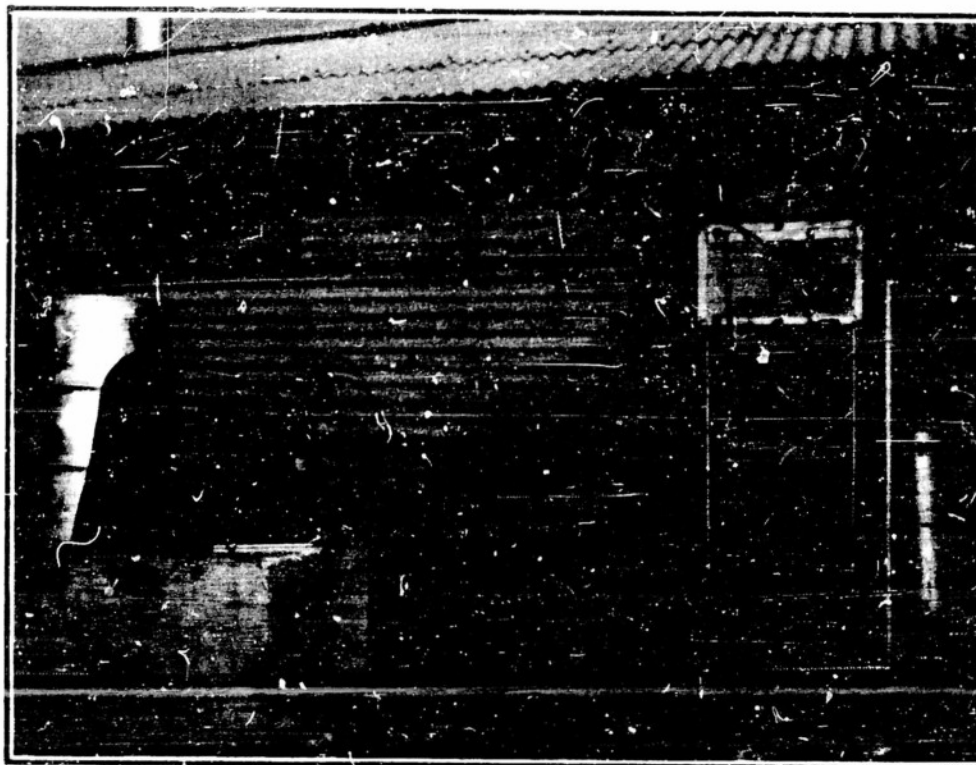


FIG. 1 LIQUID SALT TESTING APPARATUS



**FIG.2 LIQUID SALT TESTING APPARATUS**

materials that had satisfactory liquid properties were then subjected to the burner test. The burner was operated under water to test the operation before using the molten salts. Since these salts are solids at room temperature, the operation was started, when applicable, with saturated salt solutions, and as the water evaporated, more salt was added. Consequently, there was always a liquid medium in which to operate the burner. This method was adequate for the nitrate salt mixtures but was not satisfactory for handling  $B_2O_3$ . In this case after the melting pot and jet-pump were filled with the salt to be tested, an electric heater was used to melt the  $B_2O_3$  and bring it up to the operating temperature. This method of raising the bath temperature proved satisfactory. When the bath was at the right temperature, the current was turned off and the burner ignited after the propane feed was set at about  $0.16 \text{ ft}^3/\text{min}$  and the oxygen adjusted to a stoichiometric mixture. The burner was then inserted into the jet-pump. About 400 Btu/min were given off by the burner. The burner was held securely to the jet-pump by fastening the burner nut onto the pipe nipple. The flame was observed through the peep sight on the end of the burner, and the temperature was observed from an iron-constantan thermocouple. It was planned to remove the excess heat from the melting pot through the coiled copper tubing. Circulating air did not remove sufficient heat, and water did not appear safe, as the generated steam came out in violent bursts rather than a steady stream. The burner was shut off when some difficulty developed, such as the salt becoming excessively hot. These simple tests served as a screen on possible substances for the proposed heat-transfer medium.

Data, results, and discussion of the investigation to uncover a suitable non-volatile heat-transfer medium are presented below. Table III summarizes these experimental observations.

The nitrate-nitrite salt mixtures were subjected to the combustion gases while the apparatus was tested. No time was kept on these runs, as these salts were rapidly converted to their respective carbonates during the early runs. After the first run large chunks of material were seen floating in the bath that proved on a qualitative analysis to be alkali carbonates. The work with this mixture was discontinued after the mechanical system had been completely tested. The next material tried was the boron trioxide or boric acid, anhydride, bath. When anhydrous material was not used, the resulting foam as the material was heated pushed so much material out of the melting pot that the system was never ready for operation. After the electric heater was put into service, only anhydrous boric acid was used. This bath could be melted and made ready for operation fairly easily, but the  $B_2O_3$  was of such a highly viscous nature that it did not circulate properly around the combustion chamber. As the result of this, the chamber melted off, as evidenced by the recovery of small globules of metal from the  $B_2O_3$  bath. Figure 3b shows the burner with part of the combustion chamber melted off. Since no method was found to lower the operating temperature of this bath, tests were discontinued on the boron trioxide.

Halogen salt mixtures, especially the chloride salts of Li, Na, and K, appeared from the literature survey to be promising as heat-transfer media.

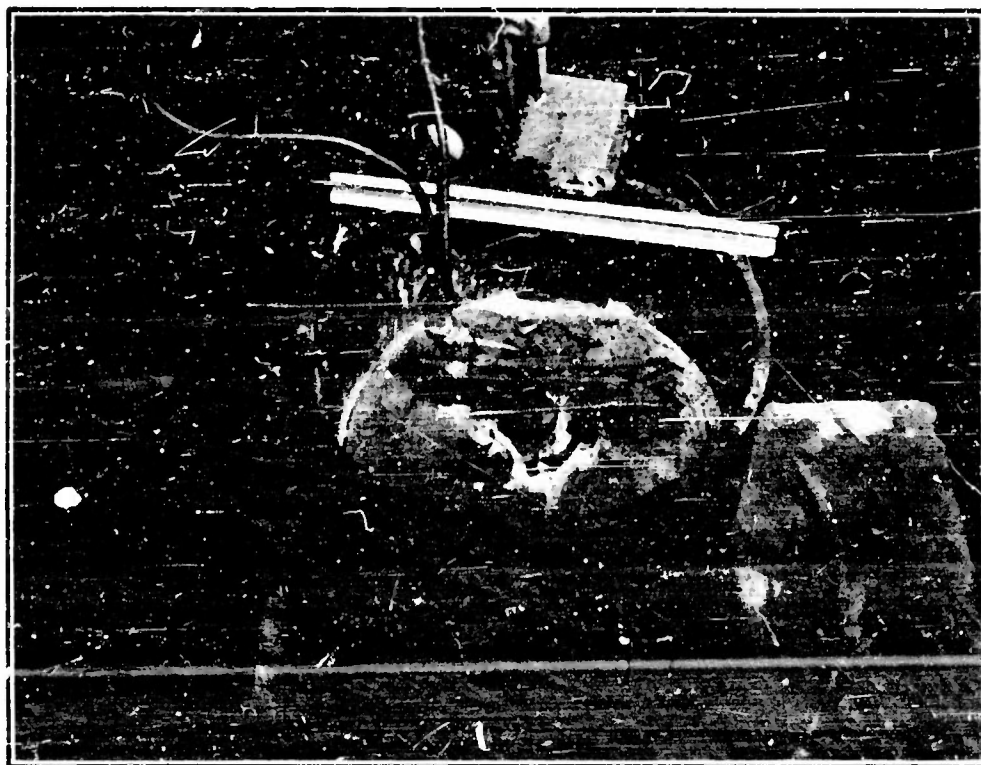


FIG. 3A LIQUID SALT TESTING APPARATUS

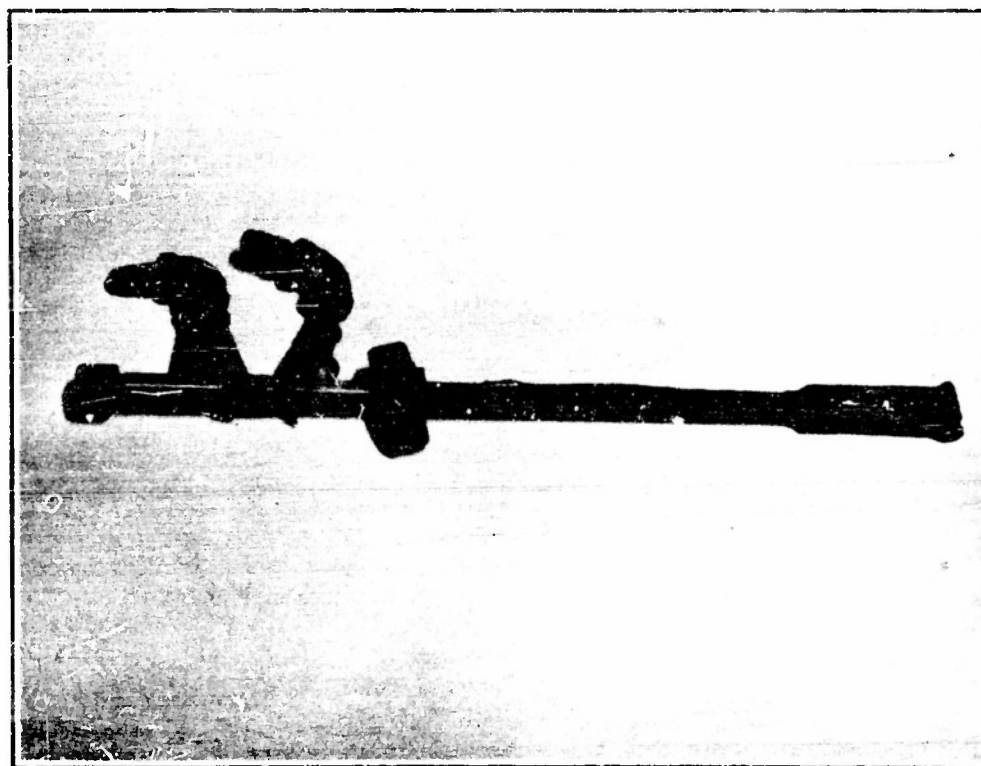


FIG. 3B DAMAGED BURNER ASSEMBLY



(4,39,43,44). The salt eutectic, 46.5 mol per cent LiCl, 42 mol per cent KCl, and 11.5 mol per cent NaCl, and also the same fluoride eutectic mixture, were melted in porcelain crucibles. The fluoride eutectic was very tacky and viscous, whereas the chloride material had greater fluidity and clarity. As a result of these tests, the chloride eutectic was chosen for subsequent testing. Approximately eight pounds of the eutectic mixture were made up and melted in the melting pot by the electric heater.

After the burner had been ignited, the combustion chamber quickly became red hot; but when it was immersed into the liquid salt, it was cooled sufficiently to allow the burner to operate until the bath reached its maximum operating temperature of 1250°F about 20 minutes later. During this 20 minutes time air to the 1/4-in. copper cooling coils was supplied at 100 psig from the compressor. Since the air did not remove heat as fast as supplied by the burner, the temperature continued to rise. At 1200°F fumes from the bath became visible, and when the burner was extinguished at 1300°F, the fumes from the bath were intense.

A preliminary calculation shows that of the 408 Btu/min entering the bath, only 240 Btu/min were carried off by the circulating air. This 168 Btu/min difference raised the temperature of the bath about 600°F in the 20 minutes if a specific heat of 0.7 Btu/lb-°F is assumed (43).

When the burner was removed, it was found to be in perfect condition, thus showing that the combustion chamber had been cooled properly by the circulating salt. After the bath had cooled, a sample of the salt was taken and dissolved in water. The pH was found to be approximately 7. This indicated no decomposition of the salt to basic materials, but rather only some volatilization of the salt mixture.

Other salt mixtures of phosphates and carbonates were melted in the porcelain crucibles, but they were found to be unsuitable for the stated purpose.

#### RECOMMENDATIONS FOR FUTURE WORK

The testing apparatus should be enlarged so that it may act as a calorimeter in the burning process. In this manner the parameters, specific heat, viscosity, heat-transfer coefficients, etc., of these heat-transfer media may be estimated, and the stability of the salts can be evaluated by longer running times.

Since boron trioxide is exceedingly stable over an extended temperature range, a short investigation to find some additional material that will lower its melting point and viscosity would be helpful. The thermodynamic properties of the alkali carbonates and hydroxides will be collected in order to calculate the equilibriums involved in a mixed system.

### CONCLUSIONS

It appears from this investigation to find a non-volatile heat-transfer medium suitable for a novel high-output steam generator that:

- (1) none of the organic materials nor pure elements will meet the stability and service requirements;
- (2) nitrate salt mixtures are chemically altered by the products of combustion;
- (3) boron trioxide is the most promising oxide, but because of its corrosive melt (31), high-melting point, and high viscosity it is not suitable in its pure form as the heat-transfer medium for the proposed application;
- (4) the halogen eutectics, especially the chlorides of the alkali metals, appear suitable;
- (5) equilibrium systems, such as  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Li}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ , and  $\text{LiOH}$  might be acceptable.



#### REFERENCES

- (1) Kirst, W. E., Nagle, W. M., and Castner, J. B., Trans. Am. Inst. Chem. Eng., 36, 1-20 (1940).
- (2) Moore, W. F., Coke and Gas, 12, 317-23 (1950).
- (3) Hammond, C. F., J. Inst. Fuel, 3, 302 (1930).
- (4) Hall, F. P. and Insley, H., Phase Diagrams for Ceramists, American Ceramic Society, Inc. (1947), also Part II of November, 1947, issue of the J. Am. Ceram. Soc.
- (5) O'Keefe, P., Materials and Methods, 34, 115-130 (1951).
- (6) Brewer, L., Chem. Rev., 52, 1-76 (1953).
- (7) Kracek, F. C., Morey, G. W., and Merwin, H. E., Am. J. Sci., 35-A, 143-71 (1938).
- (8) Speiser, R., Naiditch, S., and Johnston, H. L., J. Am. Chem. Soc., 72, 2578 (1950).
- (9) Southard, J. C., J. Am. Chem. Soc., 63, 3147 (1941).
- (10) Jonckel, E., Z. anorg. u. allgem. Chem., 227, 214-20 (1936).
- (11) Mazelev, L. Y., Zhur. Priklad. Khim., 13, 1268-1302 (1940)(abstract in French).
- (12) Leont'eva, A. A., Zhur. Fiz. Khim., 24, 798-801 (1950).
- (13) Gmelin's Handbook of Inorganic Chemistry (German), Vol. 13 - Boron (1926).
- (14) Foex, M., Compt. rend., 212, 607-9 (1941).
- (15) Geller, R. F. and Bunting, E. N., J. Research Natl. Bur. Standards, 18, 585-93, (1937).
- (16) Eubank, R., and Bogue, R. H., J. Research Natl. Bur. Standards, 40, 225-34 (1948).
- (17) Cole, S. S., and Taylor, N. W., J. Am. Ceram. Soc., 18, 55-8 (1935).
- (18) Potts, J. C., J. Am. Ceram. Soc., 24, 43-50 (1941).
- (19) Toropov, N. A., and Koncvalov, P. F., Zhur. Fiz. Khim., 14, 1103-10 (1940).

- (20) Knight, M. A., Penna. State Coll. Abstracts, 5, 343-7 (1942).
- (21) Davis, H. M., and Knight, M. A., J. Am. Ceram. Soc., 28, 97-102 (1945).
- (22) Dane, E. B., J. Appl. Phys., 9, 669-74 (1938).
- (23) Levi, G. R., and Curti, R., Gazz. chim. ital., 68, 376-80 (1938).
- (24) Jaumes, P., and Gontard, A., Bull. soc. chim. France (5), 4, 139-48 (1937).
- (25) Jaumes, P., and Galhac, E., Bull. soc. chim. France (5), 4, 149-57 (1937).
- (26) Kobeko, P. P., Kuvshinski, S. V., and Shiskin, N. I., Leningrad Phys. Tech. Inst. Conf. on Viscosity of Liquids and Colloidal Solns., 2, 71-5 (1944).
- (27) Stalhane, B., Z. Elektrochem., 36, 404-8 (1930).
- (28) Hackspill, L., Rollet, A. P., and Andres', L., Compt. rend., 192, 48-50 (1931).
- (29) Thome, P. C. L., and Ward, A. M., Inorganic Chemistry (Fritz Ephraim), Gurney and Jackson, London (1939).
- (30) Badger, A. E., and Pittman, A. C., Ceram. Ind., 28, 216 (1937).
- (31) Lux, H., Naturwissenschaften, 28, 92 (1940).
- (32) Vargin, V. V., Optiko-Mekhan. Prom., 6, 14-16 (1936); Chem. Zentr., 1937, II, 4222.
- (33) Todd, B. J., and Miller, R. R., J. Am. Chem. Soc., 68, 530 (1946).
- (34) Roth, W. A., and Berger, E., Ber. deut. chem. Ges., 70B, 48-54 (1937).
- (35) Adadurov, I. E., Zhur. Fiz. Khim., 2, 727-34 (1931).
- (36) Guthrie, F. C., and Nance, J. T., Trans. Faraday Soc., 27, 223-33 (1931).
- (37) Kersten, J., U. S. Patent 1,692,175 (1923).
- (38) Bichowsky, F. R., Foote Prints, 8, 1-7 (1935).
- (39) Lowry, T. M., Nature 119, 564 (1927).
- (40) Glasstone, S., Thermodynamics for Chemists, D. Van Nostrand Company, Inc., New York (1947).

- (41) Domange, L., Ann. Chim. (Paris), 7, 225-97 (1937).
- (42) Holden, A. F., and Solakia, H., U. S. Patent 2,394,777 (1946).
- (43) Kayser, T., Chem. Met. Eng., 40, 353-4 (1933).
- (44) Sanders, E., German Patent 519,062 (1929).
- (45) Kangro, W., and Wieking, H. W., Z. physik. Chem., A183, 199-203 (1938).
- (46) Mayer, J. E., and Wintner, I. H., J. Chem. Phys., 6, 301-6 (1938).
- (47) Stull, D. R., Ind. Eng. Chem., 39, 540 (1947).
- (48) Janis, A. A., and Ferguson, J. B., Can. J. Research, 17, B 215-30 (1939).
- (49) Karpachev, S., Zhur. Fiz. Khim., 6, 1079-85 (1935).
- (50) Rasninskaya, I. S., and Bergman, A. G., Compt. rend. acad. sci. U. R. S. S., 38, 176 (1943).
- (51) Elchardus, E., and Laffitte, P., Bull. soc. chim. France, 51, 1572 (1932).
- (52) Olander, A., and Liander, H., Acta Chem. Scand., 4, 1437 (1950).
- (53) Leitgeb, W., Metallwirtschaft, 11, 699-700 (1932).
- (54) Keitel, H., Neues Jahrb. Mineral. Geol., Beilage Bd., 52A, 378-423 (1925).
- (55) Johnson, C. R., J. Phys. Chem., 39, 791-5 (1935).
- (56) Ipatov, I. V., Zhur. Fiz. Khim., 5, 790-2 (1934).
- (57) Villa, H., J. Soc. Chem. Ind. London, Supplementary Issue No. 1, 39-513 (1950).
- (58) Satô, T., and Amano, T., Kinzoku-no-Kenkyu, 11, 305-16 (1934).
- (59) S(hearon), W. H., Ind. Eng. Chem., 45, 15A-18A, June (1953).
- (60) Samuel, Mitt. Kali-Forsch. Anstalt, 1923, 103-5.
- (61) Salstrom, E. J., J. Am. Chem. Soc., 53, 3385-9 (1931).
- (62) Bergman, A. G., and Dergunov, E. P., Compt. rend. acad. sci. U. R. S. S., 31, 754 (1941).
- (63) Alexander, J., and Hider, S. G., Ind. Eng. Chem., 39, 1044-9 (1947).

- (64) Eitel, W., and Skaliks, W., Z. anorg. u. allgem. Chem., 103, 263 (1929).
- (65) Anon., Fluorochemicals, Minnesota Mining and Manufacturing Co., St. Paul 6, Minn.
- (66) Lyon, R. N., Liquid Metals Handbook, Atomic Energy Commission, Department of the Navy, Washington, D. C., June (1952).

TABLE I

COMPILATION OF PROMISING SUBSTANCES

	<u>Melting Point OF</u>	<u>Temp. at which vapor pressure is 10<sup>-3</sup> atm., OF</u>	<u>Remarks</u>
Nitrate-Nitrite Eutectic	288	1050	Commercially available, low melting point
Boron Trioxide	842	2200	Stable, low vapor pressure, high vis- cosity, corrosive (6, 31)
Chloride Eutectic	650	1000	Low hydrolysis constant, low viscosity, good heat conductor, long liquid range
Fluoride Eutectic	850	-	High viscosity, high melting point, low hy- drolysis constant, stable
Carbonate Eutectic	910	-	High vapor pressure
Metaphosphates	1160	-	Corrosive to metals and refractories, high melt- ing points, stable to combustion gases

TABLE II

RESULTS OF THE INDUSTRIAL SURVEY

## Part A: High Temperature Liquid Systems

<u>Organization</u>	<u>Results</u>
Aluminum Co. of America Philadelphia, Pa.	They suggested the use of gallium and supplied detailed information on it.
American Cyanamid Co. New York 20, N. Y.	They suggested the use of their nitrate-nitrite salt mixture. Information on the mixture was included.
The Atlantic Refining Co. Philadelphia, Pa.	They suggested the use of their heat-transfer oils and supplied information about them.
Battelle Memorial Institute Columbus, Ohio	They sent a steel publication for reference on the subject.
Bethlehem Foundry & Mach. Co. Bethlehem, Pa.	They supplied details on their Beth-Tec system using a nitrate-nitrite salt mixture.
Crown Chemical Corp. Branford, Conn.	They supplied details and recommended their nitrate-nitrite salt mixture.
Esso Chemical Corp. Weehawken, N. J.	They supplied details and recommended their nitrate-nitrite salt mixture.
E. I. du Pont de Nemours Co. Charlotte, N. C.	They supplied details and recommended their nitrate-nitrite salt mixture.
Harshaw Chemical Co. Cleveland, Ohio	They had no materials available.
Holden, A. F., Company New Haven, Conn.	They supplied details and recommended their nitrate-nitrite salt mixtures.
Houdry Process Corp. Philadelphia, Pa.	They supplied details and recommended their nitrate-nitrite salt mixtures.
Houghton, E. F. Company Philadelphia, Pa.	They supplied details and recommended their nitrate-nitrite salt mixtures.

TABLE II (continued)

<u>Organization</u>	<u>Results</u>
Mallinckrodt Chem. Co. New York, N. Y.	They suggested such materials as Wood's metal, sodium, sodium dichromates, etc.
Mitchell-Bradford Chem. Co. Stratford, Conn.	They suggested and sent details on their nitrate-nitrite salt.
Park Chemical Co. Detroit, Mich.	They suggested and sent details on their nitrate-nitrite salt.
Socony-Vacuum Oil Co. New York, N. Y.	They suggested contacting the Houdry Corp., as they had no available information.
Sun Oil Co. Philadelphia, Pa.	They suggested and supplied details on their heat-transfer oils.
United States Steel Co. Kearny, N. J.	They suggested such materials as lead, lead alloys, and nitrate-nitrite salt mixtures.

## Part B: Equipment or Materials of Construction

Ajax Electric Co. Philadelphia, Pa.	Brochure sent which tells of their equipment suitable for different temperature ranges.
American Gas Furnace Co. Elizabeth, N. J.	Catalogue sent which tells of their equipment suitable for different temperature ranges.
American Locomotive Co. New York 8, N. Y.	Letter sent which tells what type steel to use at different temperature levels with the nitrate-nitrite bath.
Bellis Company Branford, Conn.	Letter sent which tells what type steel to use at different temperature levels with the nitrate-nitrite bath.
Struthers-Wells Corp. Philadelphia, Pa.	Brochure sent which tells of their operations.
Upton Electric Salt Bath Furnace Co. Detroit, Mich.	Brochure sent which tells of their operations.

TABLE II (continued)

Part C: Special Chemicals

<u>Organization</u>	<u>Results</u>
Blockson Chemical Co. Joliet, Ill.	They discouraged the use of molten phosphate salts because of the corrosion problems.
Bureau of Mines Berkeley, Calif.	They sent references to the available information oxide systems.
Foots Mineral Co. Philadelphia, Pa.	They sent information on their lithium salts.
Minnesota Mining & Mfg. Co. St. Paul, Minn.	They sent a brochure describing their fluorochemicals.
Pacific Coast Borax Co. New York 17, N. Y.	They supplied data and samples of boron trioxide and boric acid.

Part D: Submerged Combustion Units

Chemical Construction Corp. New York, N. Y.	They had no available information.
Dixie Chemical Co. Houston, Texas	They referred us to others, as they had no available information.
Kemp, C. M., Manufacturing Co. Baltimore, Md.	They had no available information.
Ozark-Mahoning Co. Tulsa, Oklahoma	They sent brochures and details on their commercial submerged combustion units.
Submerged Combustion Co. of America Hammond, Ind.	They sent details, letters, and brochures on their laboratory and commercial units.

Part E: Safety

National Board of Fire Underwriters New York, N. Y.	They sent their report on how to handle safely the liquid salt baths.
--	---



TABLE III

EXPERIMENTAL EVALUATION OF MATERIALS

<u>Material</u>	<u>Crucible Test</u>	<u>Burner Test</u>
Nitrate-Nitrite Salt	Clear, non-fuming liquid of low viscosity	Reacted with the product carbon dioxide and formed carbonates.
Boron Trioxide	Viscous, non-fuming material	It is too viscous and does not conduct heat well at 900°F. Combustion chamber melted.
Chloride Eutectic	Clear, non-fuming liquid of low viscosity	Circulated satisfactorily in the testing apparatus and did not fume until it reached 1250°F.
Fluoride Eutectic	Tacky, viscous-type material that developed fuming hot spots	Test was not run.
Carbonate Eutectic	Fumed excessively	Test was not run.
Metaphosphates	Did not become a true liquid as the temperature did not get high enough.	Test was not run.

# DISTRIBUTION LIST

<u>Copy No.</u>		<u>Copy No.</u>	
1-2	Chief of Naval Research Department of the Navy Washington 25, D. C. Attn: Code 429	15-19	Armed Services Technical Information Agency Document Service Center Knott Building Dayton, Ohio
3-8	Director Naval Research Laboratory Washington 25, D. C. Attn: Technical Information Officer	20	Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 551
9	Commanding Officer Office of Naval Research Branch Office Tenth Floor The John Crerar Library Bldg. 86 East Randolph Street Chicago 1, Illinois	21	Commanding Officer and Director U. S. Naval Engineering Experiment Station Annapolis, Maryland
10	Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York	22	Commanding Officer and Director U. S. Naval Boiler and Turbine Laboratory Naval Base Philadelphia, Pennsylvania
11	Commanding Officer Office of Naval Research Branch Office 1030 East Green Street Pasadena 1, California	23	Office of Technical Services Department of Commerce Washington 25, D. C.
12	Commanding Officer Office of Naval Research Branch Office 1000 Geary Street San Francisco 9, California	24	Naval Inspector of Ordnance Applied Physics Laboratory 8621 Georgia Avenue Silver Spring, Maryland
13-14	Officer-in-Charge Office of Naval Research Navy #100 Fleet Post Office New York, New York	25-40	Experiment Incorporated Reserve